

Unified description of hydrogen bonding and proton transfer by a two-state effective Hamiltonian

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An effective Hamiltonian is considered which describes hydrogen bonding and proton transfer between two molecules due to the quantum mechanical interaction between the orbitals of the H-atom and of the donor (D) and acceptor (A) atoms in the molecules. The Hamiltonian acts on two diabatic states and has a simple chemically motivated form for its matrix elements. The model gives insight into the "H-bond puzzle", describes different classes of bonds, and empirical correlations between the donor-acceptor distance R and binding energies, D-H bond lengths, and the softening of D-H vibrational frequencies. A key prediction is the UV photo-dissociation of H-bonded complexes via an excited electronic state with an exalted vibrational frequency.

Hydrogen bonds play a key role in a diverse range of phenomena in physics, chemistry, molecular biology, and materials science. For example, hydrogen bonding is central to the unique properties of water, to protein folding and function, to proton transport [1], to corrosion [2], and to aspects of crystal engineering. Hydrogen bonds have properties that are distinctly different from other chemical bonds. Many properties are poorly understood and recently the International Union of Pure and Applied Chemistry gave a new definition [4], particularly motivated by the occurrence of hydrogen bonding to a wide range of atoms other than oxygen (e.g., fluorine, carbon, nitrogen) and a wide range of bond lengths and energies. Gilli and Gilli have emphasized "the H-bond puzzle" which is stated as "the unique feature of the H-bond is that bonds made by the same donor-acceptor pair may display an extremely wide range of energies and geometries" [5]. A wide range of empirical correlations have been observed between different physical properties including bond lengths, binding energies, shifts in vibrational frequencies, vibrational absorption intensity, and NMR chemical shifts [5, 6].

In this Letter, I consider a simple effective two state Hamiltonian for a hydrogen bond between a donor denoted D-H and an acceptor, which form a complex, denoted D-H...A. The Hamiltonian provides insight into the H-bond puzzle, gives a single description of different classes of H-bonds, and provides a semi-quantitative description of observed empirical correlations. The key independent variable (or physico-chemical "descriptor") is the distance between the donor and acceptor R (see Figure 1).

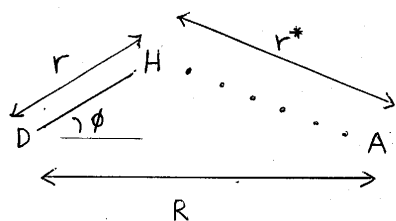


Figure 1. (Color online.) Definition of geometric variables for a hydrogen bond between a donor D and an acceptor A.

Reduced Hilbert space for the effective Hamiltonian. Dia-

batic states [8] (including valence bond states) have proven to be a powerful method of developing chemical concepts [9, 10]. Previously it has been proposed that hydrogen bonding and hydrogen transfer reactions can be described by an Empirical Valence Bond model [11–16] involving valence bond states. Here, I choose a basis consisting of two diabatic states which can be denoted as $|D-H, A\rangle$ and $|D, H-A\rangle$. The latter represents a product state of the electronic states of a D atom and of a H-A bond in the absence of the D atom. These involve D-H and H-A bonds which have both covalent and ionic components, the relative weight of which depends on the distance r . The Morse potentials (see below) capture the associated energetics including the partial electrostatic character of the H-bond.

Effective Hamiltonian. The Hamiltonian for the diabatic states will have matrix elements which depend on the D-H bond length r , the donor-acceptor separation R , and the angle ϕ which describes the deviation from linearity (compare Figure 1). The functional dependence can be parametrised from quantum chemistry calculations [12]. However, the parameters may depend significantly on the level of theory used. The main point of this Letter is that one can obtain both a qualitative and semi-quantitative description of hydrogen bonding using a simple and physically transparent parametrisation of these matrix elements. This approach highlights the quantum mechanical (covalent) character of the H-bond [7] and unifies H-bonding involving different atoms and weak, medium, and strong (symmetrical) H-bonds. The latter are sometimes characterised as covalent 4 electron, 3 centre bonds [9]. The model Hamiltonian has the advantage that it is straightforward to extend it to describe nuclear quantum effects (including going beyond the Born-Oppenheimer approximation), multiple H-bonds, and collective effects.

The Morse potential describes the energy of a single bond within one of the molecules in the absence of the second (and thus the diabatic states). The two cases $j = D, A$ denote the donor D-H bond and acceptor A-H bond, respectively. The Morse potential is

$$V_j(r) = D_j [\exp(-2a_j(r-r_{0j})) - 2\exp(-a_j(r-r_{0j}))] \quad (1)$$

where D_j is the binding energy, r_{0j} is the equilibrium bond length, and a_j is the decay constant. The harmonic vibrational frequency ω is given by $\mu\omega^2 = 2D_j a_j^2$ where μ is the reduced

mass. [For O-H bonds, $\omega \simeq 3600 \text{ cm}^{-1}$, $D \simeq 120 \text{ kcal/mol}$, $a \simeq 2.2/\text{\AA}$, $r_0 \simeq 0.96\text{\AA}$.] A simple harmonic potential is not sufficient because the O-H bond is highly anharmonic and we will be interested in regimes where there is considerable stretching of the bonds.

I take the effective Hamiltonian describing the two interacting diabatic states to have the form

$$H = \begin{pmatrix} V_D(r) & \Delta_{DA}(R, \phi) \\ \Delta_{DA}(R, \phi) & V_A(r^*) \end{pmatrix} \quad (2)$$

where the diabatic states are coupled via the matrix element

$$\Delta_{DA}(R, \phi) = \Delta_0 \cos(\phi) \frac{(R - r \cos \phi)}{r^*} \exp(-bR) \quad (3)$$

where $r^* = \sqrt{R^2 + r^2 - 2rR \cos \phi}$ is the length of the A-H bond (see Figure 1), and b defines the decay of the matrix element with increasing R . This functional dependence on R and ϕ can be justified from that for orbital overlap integrals [17] together with a valence bond theory description of 4 electron 3 orbital systems [9]. With regard to the angular dependence I have assumed that the σ overlap dominates the π overlap. Roughly Δ_{DA} is the overlap of the hybrid (s and p) orbitals on the D and A atoms and there will be some variation in the parameters Δ_0 and b with the chemical identity of the atoms D and A. For the rest of the paper I focus on the case of linear H bonds ($\phi = 0$) and (3) can be written as

$$\Delta(R) = \Delta_1 \exp(-b(R - R_1)) \quad (4)$$

where R_1 is a reference distance, $R_1 \equiv 2r_0 + 1/a$.

Potential energy surfaces. In the adiabatic limit the energy eigenvalues are

$$E_{\pm}(r, R) = \frac{1}{2}(V_D(r) + V_A(R - r)) \quad (5)$$

$$\pm \frac{1}{2} \left((V_D(r) - V_A(R - r))^2 + 4\Delta(R)^2 \right)^{\frac{1}{2}}. \quad (6)$$

I now focus on the symmetric case $D = A$ and return to the asymmetric case briefly at the end of the paper.

Figure 2 shows the adiabatic energy eigenvalues (potential energy curves) $E_{-}(r, R)$ and $E_{+}(r, R)$ as a function of r , for three different fixed R values. Note three qualitatively different curves, corresponding to weak, moderate, and strong hydrogen bonds. For moderate bonds (corresponding to $R \simeq 2.6\text{\AA}$ for an O-H...O system) the energy barrier becomes comparable to the zero point energy of the diabatic states, $\hbar\omega/2 \simeq 1800 \text{ cm}^{-1} \sim 0.04D$. Hence, for smaller R quantum nuclear effects become important. The lowest curve in Figure 2 shows a ground state potential energy surface which has an extremely flat bottom, as is observed in quantum chemistry calculations for H_3O_2^- and H_5O_2^+ [18].

The value of $\Delta_1 = 0.4D \simeq 2 \text{ eV}$ used here for O-H...O systems is estimated from comparisons of the model predictions with experimental H-bond energies (see Figure 5 below) and vibrational frequencies (Figures 6 and 7) [19]. This is a relatively large interaction between the diabatic states, and is

comparable to values estimated from quantum chemical calculations at the MP2 level [12]. The competition between this large energy scale and the large energies of stretched bonds is key to understanding H-bond properties.

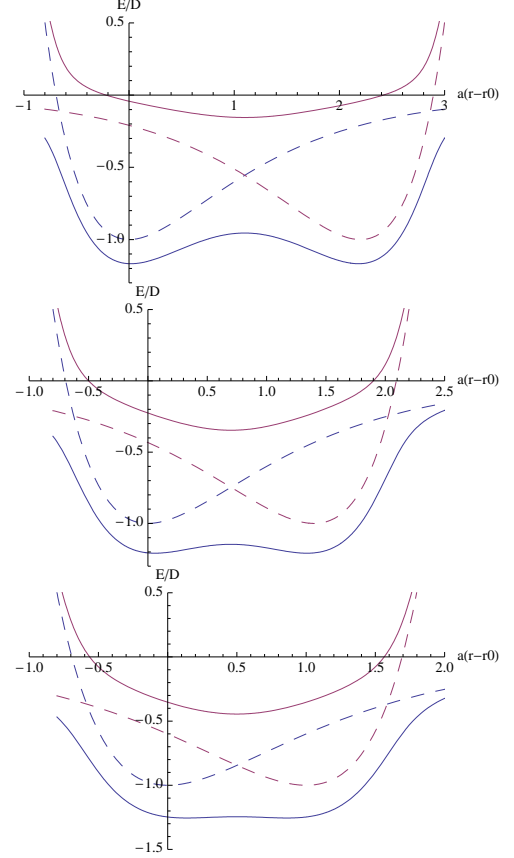


Figure 2. (Color online.) Potential energy curves for the diabatic and adiabatic states of a symmetric hydrogen bonded system. The horizontal axis is proportional to the difference between the length of the D-H bond, r , and its isolated value, r_0 . The vertical energy scale is D , the binding energy of an isolated D-H bond. All adiabatic curves are for $\Delta_1 = 0.4D$ and $b = a$. The diabatic curves (dashed lines) are Morse potentials centred at $r = r_0$ and $r^* = R - r_0$ and correspond to isolated D-H and H-A bonds, respectively. For parameters relevant to a O-H...O system the three sets of curves correspond (from top to bottom) to oxygen atom separations of $R = 2.9, 2.6$, and 2.3 \AA , respectively, characteristic of weak, moderate (low barrier), and strong hydrogen bonds [5]. An important prediction of this model is the existence of the excited state with energy $E_{+}(r, R)$ (upper curve).

Insight into the H-bonding puzzle. Figures 3, 4, 5 show that varying R between 2.4\AA and 3.0\AA can lead to a wide range of D-H bond lengths and hydrogen bond energies. In an actual H-bonded complex the equilibrium R value will be determined by the total energy which includes contributions from the potential surface shown in Figure 3 and other interactions not included in this model. Possible interactions include electrostatic interactions between the donor and acceptor, steric effects, and van der Waals interactions. In large molecules with intramolecular hydrogen bonding R may actually be determined largely by the skeletal geometry in which the donor

and acceptor atom are imbedded. Similarly, in water-hydroxyl overlayers on metal surfaces, the distance R is largely determined by the lattice constant of the substrate [2]. This provides insight into the origin of the H-bond puzzle because the identity of the donor and acceptor atoms determines the Hamiltonian parameters except R , whose equilibrium value will be determined by residual interactions.

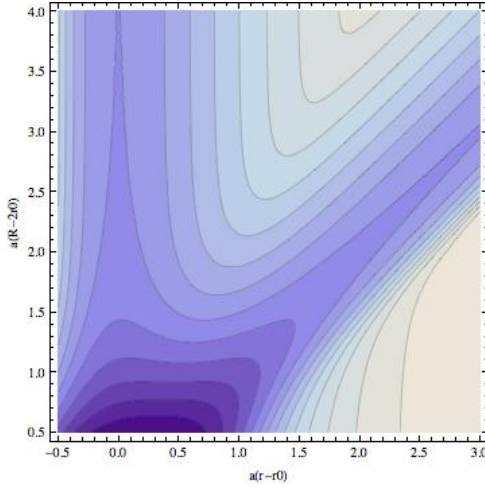


Figure 3. (Color online.) Contour plot of the ground state potential energy surface (for a symmetric donor acceptor-system) as a function of the D-H bond length $a(r - r_0)$ (horizontal axis) and the donor-acceptor distance $a(R - 2r_0)$ (vertical axis). Note that as R varies a wide range of equilibrium bond lengths $r_m(R)$ are possible. For this plot $\Delta_1 = 0.4D$ and $b = a$. The contour spacing is $0.07D$ and darker shades represent lower energies.

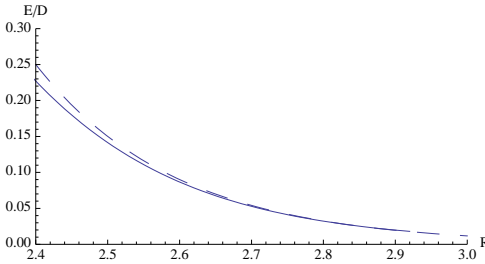


Figure 4. (Color online.) Correlation between the H-bond energy and donor-acceptor distance R (in Å). Solid line is for the model Hamiltonian with $b = a = 2.2/\text{Å}$, $\Delta_1 = 0.4D$. The dashed curve is an empirical relation, $E_{HB} = E_{max} \exp(k(R_0 - R))$ with $k = 5.1$, $R_0 = 2.4\text{Å}$, and $E_{max} = 27 \text{ kcal/mol} = 0.25D$ for O-H...O bonds[5].

H-bond energies. Figure 4 shows a favourable comparison between the calculated binding energies as a function of R with an empirical relation for O-H...O bonds [5].

Bond lengths. In the adiabatic limit, the equilibrium D-H bond length r for a fixed R , is determined by the minimum of $E_-(r, R)$ (see Figure 5). With decreasing R the D-H bond length increases from its non-interacting value $r_0 \simeq 0.96\text{Å}$ to $R/2$ for a symmetric bond associated with a barrierless

potential well. Figure 5 shows that the bond lengths calculated from the minimum of $E_-(r, R)$ are significantly less than those observed experimentally for $R \leq 2.6\text{Å}$. This difference is attributed to the importance of quantum nuclear effects which become when the energy barrier is comparable to the zero point energy of the D-H stretch vibration. A signature of such quantum effects are isotope effects. Indeed this can be seen by comparing the crystal structure of CrHO_2 and CrDO_2 ; in the former the O-H-O bond appears to be symmetric and $R = 2.49 \pm 0.02\text{Å}$, whereas the O-D-O bond is asymmetric with an O-D bond length of $0.96 \pm 0.04\text{Å}$, with $R = 2.55 \pm 0.02\text{Å}$ [20].

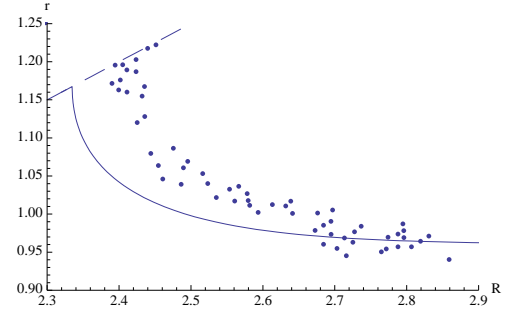


Figure 5. (Color online.) Correlation between the D-H bond length r and the D-A distance R . Both lengths are in units of Å. The solid curves is the bond length deduced from the minimum of the adiabatic potential for $b = a$ and $\Delta(R) = 0.4D$. For the moderate to strong H-bonds which occur for $R < 2.5\text{Å}$ quantum nuclear motion will significantly increase the D-H bond length because the energy barrier becomes comparable to the zero point energy. The dots are experimental data for O-H...O bonds in a wide range of crystal structures and are taken from Figure 6 in [22]. The dashed line corresponds to symmetric bonds ($r = R/2$).

Vibrational frequencies. As the distance R decreases there is a significant softening of the frequency of the D-H stretch vibration. In the adiabatic limit this frequency is given by the curvature at the bottom of the potential $E_-(r, R)$ (see Figure 6). The latter has been proposed as a measure of the strength of an H-bond [3]. Generally, it is expected that when the quantum nuclear motion is taken into account the actual vibrational frequency will be less than adiabatic harmonic frequency.

A key prediction of the model. The energy eigenvalue $E_+(r, R)$ describes the potential energy curve of a low lying excited state (see Figure 2) which reflects the quantum mechanical character of the H-bond. This state would not exist if the H-bond is purely classical and electrostatic. This "twin excited state" is the analogue of the $^1B_{2u}$ state in benzene, of the 1B_2 state in semibulvalene [9], and of the low-lying electronic state in the Creutz-Taube ion associated with delocalized mixed valence [21]. Hence, for strong hydrogen bond complexes there should be an electronic excited state with energy of approximately $2\Delta \sim 4 \text{ eV}$ (corresponding to a wavelength of about 300 nm). The transition dipole moment is approximately equal to twice the ground state dipole moment of an isolated OH bond, $2\vec{d}_{OH} \sim 2 \text{ Debye}$, suggested a

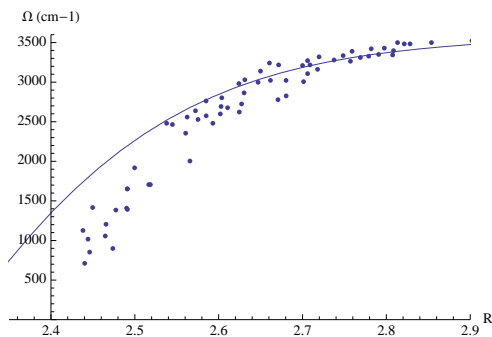


Figure 6. (Color online.) Softening of the D-H stretch frequency Ω (in cm^{-1}) with decreasing donor-acceptor distance R (in \AA). Solid line is the harmonic frequency for the model Hamiltonian with $b = a$ and $\Delta_1 = 0.4D$. The dots are experimental data for a wide range of complexes and are taken from Figure 4 in Ref. 6.

significant absorption intensity. The curve $E_+(r, R)$ has only a single minimum as a function of r and so in this excited state the H-atom will be delocalised between the donor and acceptor. For strong bonds the curvature of the adiabatic potential of the excited state is clearly larger than that of the ground state. Hence, the corresponding vibrational frequency will be larger than in the ground state, as it is in benzene and semibulvalene [9]. The intensity of the transition will be reduced by Franck-Condon factors describing the overlap of the nuclear wave functions in the ground and excited state. For weak bonds these overlaps may be small. Since $\Delta(R)$ decreases with increasing R the energy of this excited state will also decrease with increasing R , implying that exciting to this state will lead to photo-dissociation of the H-bond. I am unaware of any experimental investigations that have looked for this excited state in the UV.

Asymmetric bonds. We now consider the case where the proton affinity (PA) of the donor (D_D) and of the acceptor (D_A) are unequal, i.e., $\epsilon \equiv D_D - D_A \neq 0$. Gilli and Gilli [5] have noted the “PA, pK_a equalisation principle”: the strongest hydrogen bonds occur when the donor and acceptor have the same proton affinity. This occurs naturally in our two-state Hamiltonian. For example, for very short D-A distances and large Δ , the H-bond energy is approximately, $\epsilon - \sqrt{\epsilon^2 + \Delta^2}$, which has its largest value for $\epsilon = 0$. Figure 7 shows the softening of the D-H stretch frequency as a function of ϵ , compared to experimental data [23].

Quantum and isotope effects. The above discussion treated the nuclear degrees of freedom classically, but noted that quantum nuclear effects may have a significant effect on equilibrium bond lengths, particular for strong H-bonds. Significant isotope effects are observed experimentally [6] and arise due to the zero point motion of the hydrogen atom. Furthermore, quantum nuclear effects may play an important role in water [24], in water-hydroxyl overlayers on metal surfaces [2], and in some proton transfer reactions in enzymes [25]. For strong bonds where the potential is very anharmonic quantum nuclear effects will also be important [3]. The model

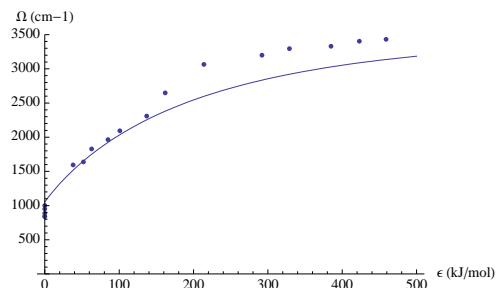


Figure 7. (Color online.) Softening of the D-H stretch frequency Ω (in units of cm^{-1}) with decreasing difference between the proton affinity of the acceptor and the donor (ϵ in units of kJ/mol). The solid line is the harmonic frequency of the model Hamiltonian with $R = 2r_0 + 1/a \simeq 2.4\text{\AA}$, $\Delta_1 = 0.4D_A$, $D_A = 120 \text{ kcal/mol}$. The dots are experimental data [23].

Hamiltonian provides a natural means to describe these effects if the the hydrogen atom co-ordinate r is treated quantum mechanically. The harmonic limit corresponds to a spin-boson model which has an analytical solution in terms of continued fractions [27]. The fully quantum Morse potential has an exact analytical solution and an algebraic representation in terms of creation and annihilation operators [28]. Hence, an algebraic treatment of the quantum version of the model Hamiltonian may also be possible, because the off-diagonal terms are independent of r .

In conclusion, the relatively simple effective Hamiltonian considered here provides a unified picture of a range of phenomena associated with hydrogen bonding. Furthermore, it predicts an excited state which should lead to photo-dissociation of an H-bonded complex. Future work could consider non-linear bonds and the associated vibrational bending modes, and correlations between R and vibrational absorption intensities and NMR chemical shifts. It would be worthwhile to provide a more rigorous justification of the diabatic state Hamiltonian from quantum chemistry. This may be done in a similar systematic manner as has been done for the excited states of the chromophore of the Green Fluorescent Protein [26].

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- [1] T.C. Berkelbach, H.-S. Lee, and M.E. Tuckerman, Phys. Rev. Lett. **103**, 238302 (2009).
- [2] X.-Z. Li et al., Phys. Rev. Lett. **104**, 066102 (2010).
- [3] X.-Z. Li, B. Walker, and A. Michaelides, Proc. Nat. Acad. Sci. (USA) **108**, 6369 (2011).

- [4] G. Desiraju, *Angew. Chem. Int. Ed.* **50**, 52 (2010).
- [5] G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond* (Oxford, 2009).
- [6] T. Steiner, *Angew. Chem. Int. Ed.* **41**, 48 (2002).
- [7] E.D. Isaacs et al., *Phys. Rev. Lett.* **82**, 600 (1999).
- [8] T. Pacher, L.S. Cederbaum, and H. Köppel, *J. Chem. Phys.* **89**, 7367 (1988); T. Van Voorhis et al., *Ann. Rev. Phys. Chem.* **61**, 149 (2010).
- [9] S.S. Shaik and P.C. Hiberty, *A Chemists Guide to Valence Bond Theory* (Wiley, 2007).
- [10] P. Politzer, J.R. Reimers, J.S. Murray, and A. Toro-Labb, *J. Phys. Chem. Lett.* **1**, 2858 (2010).
- [11] R. Vuilleumier and D. Borgis, *J. Mol. Struct.* **436**, 555 (1997).
- [12] D.E. Sagnella and M. E. Tuckerman, *J. Chem. Phys.* **108**, 273 (1998).
- [13] J. Florian, *J. Phys. Chem. A* **106**, 5046 (2002).
- [14] C. Coulson and U. Danielsson, *Arkiv Fysik* **8**, 245 (1954).
- [15] A. Warshel and R.M. Weiss, *J. Am. Chem. Soc.* **102**, 6218 (1980); A. Warshel, *Computer modeling of chemical reactions in enzymes and solutions* (Wiley, 1991).
- [16] A similar diabatic state formulation is implicit in the seminal paper, "Outlines of a theory of proton transfer," J. Horiuti and M. Polanyi, *Acta Physicochimica U.R.S.S.* **2**, 505 (1935). [A translation is reprinted in *J. Molecular Catalysis A: Chemical* **199**, 185 (2003).]
- [17] R.S. Mulliken, C.A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.* **17**, 1248 (1949).
- [18] M. Kowal, S. Roszak, and J. Leszczynski, *J. Chem. Phys.* **114**, 8251 (2001).
- [19] It can be shown that the condition for no energy barrier in the ground state is
- $$\frac{\Delta(R)}{D} \geq \frac{(1 - \exp(-\mu))^2}{1 - \frac{1}{2} \exp(\mu)} \quad (7)$$
- where $\mu \equiv a(R/2 - r_0)$ [19]. This leads to a symmetric D-H-A bond in the adiabatic limit where the nuclear degrees of freedom are treated classically. Empirical correlations [5] suggest that for O-H-O complexes symmetric bonds occur when $R \simeq 2.4\text{\AA}$. Using $a \simeq 2.2/\text{\AA}$, $r_0 = 0.96\text{\AA}$ gives $\mu = 0.52$ the above expression gives $\Delta(R) \simeq D$. For short bonds (i.e., $\mu \ll 1$) the right hand side the above expression reduces to $2\mu^2$ (harmonic limit) which for $\mu = 0.52$ gives $\Delta \simeq 0.6D$, significantly different from the value above, showing the importance of anharmonic effects.
- [20] W.C. Hamilton and J.A. Ibers, *Acta Cryst.* **16**, 1209 (1963).
- [21] L.K. McKemmish, R.H. McKenzie, N.S. Hush, and J.R. Reimers, arXiv:1107.1105.
- [22] P. Gilli et al., *J. Am. Chem. Soc.* **116**, 909 (1994).
- [23] J. R. Roscioli, L. R. McCunn and M. A. Johnson, *Science* **316**, 249 (2007).
- [24] J.A. Morrone and R. Car, *Phys. Rev. Lett.* **101**, 017801 (2008).
- [25] J. Bothma, J. Gilmore, and R.H. McKenzie, *New J. Phys.* **12**, 055002 (2010), and references therein.
- [26] S. Olsen and R.H. McKenzie, *J. Chem. Phys.* **130**, 184302 (2009).
- [27] S. Paganelli and S. Ciuchi, *J. Phys.: Cond. Matt.* **18**, 7669 (2006).
- [28] F. Iachello and R.D. Levine, *Algebraic Theory of Molecules* (Oxford, 1995), Section 2.8.